Theoretical investigation of the effect of strain on phase separation in epitaxial layers

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We have theoretically investigated the phenomenon of alloy clustering in epitaxial films and, in particular, the case of $Al_xGa_{1-x}As$ grown epitaxially on GaAs. We show in the general case that the elastic strain in the film, caused by the finite mismatch between the lattice parameters of the film and the substrate, may change the miscibility properties of the film. A miscibility gap could be opened in the material composing the film, even if there is no such gap in the bulk material. Conversely, the strain could stabilize a solid solution in the film in cases where there is a miscibility gap in the bulk material of which the film is composed. We estimate that these effects are too small to account for phase separation in the case of $Al_xGa_{1-x}As$ on GaAs, but could be important in other systems, such as In(As, Sb).

I. INTRODUCTION

Devices consisting of epitaxial layers of $Al_xGa_{1-x}As$ grown on GaAs substrate have gained prominence in electronic and optoelectronic research.[1] In many cases, the performance of such devices depends on controlling the composition of the epitaxial layer (the x in $Al_xGa_{1-x}As$). In recent years, several experimental papers have been published, indicating that under certain growth conditions, the composition of the epitaxial layer is not uniform. Holonyak *et al.*[2] observed photoluminescence features that were compatible with alloy clustering in MOCVD samples of $Al_xGa_{1-x}As$ grown on GaAs. Petroff *et al.*[3] have observed alternating layers of Al- and Ga-rich $Al_xGa_{1-x}As$ in MBE samples grown on GaAs(110). These layers were parallel to the interface, about 100 Å thick, and the variation in composition was estimated by Petroff *et al.* to be at least 5%. These results are somewhat surprising in light of the fact that bulk $Al_xGa_{1-x}As$ is known not to have a miscibility gap.[4]

Several possible mechanisms could lead to the clustering in the epitaxial layer. First, the relatively low growth temperature suggests that the observed clustering could be metastable; that would not explain how the clustering forms, only why it is observed. Second, the observed clustering could be stable in bulk $Al_xGa_{1-x}As$ at low temperatures, and the thermodynamical data (obtained from high temperature experiments) should be reevaluated for low temperatures. Third, the clustering was only observed in thin films grown epitaxially on a GaAs substrate; the clustering may, therefore, be induced by substrate.

In this paper we examine this third possibility, namely, that the substrate induces the clustering. We investigate the effects of the strain in the film, induced by the substrate, on the miscibility properties of the film. (This mechanism was proposed by Maximov[5] to explain clustering effects in $GaAs_xP_{1-x}$.) We conclude that the strain term could, in general, change these miscibility properties, i.e., a miscibility gap could be either opened or closed by the strain. To be more specific, in the case of a particular system like $Al_xGa_{1-x}As$ on GaAs, we have to know the elastic constants of the film over the entire composition range. So far, these elastic constants have not been measured for any of the III–V ternary systems.

This paper is organized as follows. In Sec. II, following this introduction, we discuss the effects of strain on phase separation in the epitaxial layer. The treatment is rather general in that section. In Sec. III, we consider some III–V systems in which the strain in the film (induced by the substrate) may change the miscibility properties of the film. In Sec. IV, we attempt to estimate the relevant parameters for the particular case of $Al_xGa_{1-x}As$ on GaAs. Our estimates of the relevant parameters would indicate that the strain term is too small to open a miscibility gap in the $Al_xGa_{1-x}As$ film, suggesting that the observed clustering is metastable. In Sec. V, we draw conclusions based on our study.

II. EFFECTS OF STRAIN ON PHASE SEPARATION

In this section we estimate the excess free energy of an epitaxial film due to the induced elastic strain. We will show that this excess free energy may have both positive and negative second derivatives with respect to the alloy composition (in the general case of a film composed of a binary or a pseudobinary alloy). This would imply that the strain in the epitaxial layer may in some cases stabilize and in others destabilize clustering. The magnitude of this excess free energy depends on the elastic constants of the alloy, as well as on the lattice mismatch. If the lattice mismatch is too small, the extra stabilization (or destabilization) of the clustering, resulting from the elastic strain, could be negligible compared to the enthalpy and entropy of mixing. In Sec. IV, we will estimate that this is the case in $Al_xGa_{1-x}As$ grown on GaAs.

When there is a mismatch between the lattice parameters of the substrate and the film, strain effects are observed in the crystal. When the epitaxial film is very thin, it is energetically favorable for the film to be strained uniformly, such that it adopts the lattice parameters of the substrate parallel to the interface. No bonds have to be broken in this case, but the elastic strain energy accumulates as the film grows thicker and thicker. At some critical thickness, misfit dislocations

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would relieve part of this strain (see, for example, van der Merwe and Ball[6] and references therein). In our treatment here, we should only treat the case of a thin film, having no misfit dislocations.

When the film adopts the lattice parameters of the substrate, its elastic strain energy is given by Hook's law

$$\Delta E = \tfrac{1}{2} V \cdot C f^2 , \tag{1}$$

where V is the volume of the film, C is some elastic constant of the film, and f is the strain in the film. The strain energy ΔE in Eq. (1) could depend on the composition x of the alloy. For discussing phase separation, we have to consider only the second derivative of the energy with respect to composition. Constant and linear terms in composition would not alter the total energy of the system upon either separation or mixing. If the second derivative of the strain energy with respect to x is positive, the strain would drive the system toward mixing, if it is negative, toward phase separation. The strain energy is only part of the total free energy, which also includes enthalpy of formation (the linear part of the enthalpy), enthalpy of mixing (the nonlinear part), and entropy of mixing terms. Consequently, the driving toward phase separation or mixing due to strain competes with the driving toward separation or mixing due to the other terms. One can see, however, that the sign of the curvature of the free energy could sometimes be reversed by the strain term. For example, in the vicinity of coexistence points, where the curvature of the bulk free energy is zero, it is the elastic strain term that could make the difference.

In our treatment, we assume a general model of a binary, or a pseudobinary alloy, say $A_{1-x}B_x$. We further assume that this alloy is grown on a substrate consisting of one of the two materials that form the alloy (say A). In our notation, therefore, when $x = 0$ the film composition is identical to that of the substrate. The composition dependence of the strain energy comes, in this case, from the composition dependence of the three terms in Eq. (1), namely V, C, and f. Usually, the materials in question are nearly lattice matched, and, therefore, the specific volume is almost independent of composition. We shall assume, therefore, that the film volume V in Eq. (1) is independent of composition. The second term in Eq. (1), C, can be expressed in terms of the usual elastic constants of the film and depends on the crystal direction of the epitaxy. In the case of a cubic film grown on a cubic substrate, C is given by[5]

$$C = \begin{cases} 2C_{11} + 2C_{12} - \dfrac{4C_{12}^2}{C_{11}} & \text{for (100)/(100)} \\ \dfrac{12C_{44}(C_{11} + 2C12)}{C_{11} + 2C_{12} + 4C_{44}} & \text{for (111)/(111)} \end{cases} . \tag{2}$$

The composition dependence of C can be calculated from the composition dependence of C_{11}, C_{12}, and C_{44}. Finally, the composition dependence of the strain is linear, according to Vegard's law. Therefore, if Δa is the difference between the lattice parameters of the two end materials which form the alloy, then

$$\Delta E = V\left(\frac{\Delta a}{a}\right)^2 \cdot \frac{1}{2} C(x)x^2 . \tag{3}$$

In Eq. (3), the compositional dependence of the strain energy is lumped in the term $C(x)x^2$. It should be emphasized here that this term may have a second derivative with respect to x of both positive and negative sign. To demonstrate this, assume that $C(x)$ is a linear function of the composition

$$C(x) = C_0(1 - x) + C_1 x . \tag{4}$$

In that case, the second derivative of $C(x)x^2$ is also a linear function of x:

$$\frac{\partial^2}{\partial x^2}[C(x)x^2] = 2C_0(1 - x) + (6C_1 - 4C_0)x . \tag{5}$$

Therefore, in this example, $C(x)x^2$ always curves upward for small values of x but may curve downward near $x = 1$ if the slope of $C(x)$ is negative enough ($C_1 < \frac{2}{3} C_0$).

III. TERNARY III–V SYSTEMS

As we have mentioned in the previous section, the energy term due to strain in the film has to compete with the bulk terms (enthalpy and entropy of mixing) in the film material. While exact numbers are not available in most cases, we would like to estimate the order of magnitude of each of these terms.

The entropy-of-mixing term dominates the free energy at high temperatures. In many of the III–V ternary systems, the entropy of mixing can be approximated by assuming that the solution is ideal:

$$S_m = -Nk\,[x \log x + (1 - x)\log(1 - x)] , \tag{6}$$

where N is the number of formula units. Taking the second derivative of Eq. (6) with respect to concentration

$$\frac{\partial^2 S_m}{\partial x^2} = -Nk\left[\frac{1}{x} + \frac{1}{1 - x}\right] < -4Nk . \tag{7}$$

$4kT$ is approximately 300 meV at 600 °C. This term is, therefore, quite large at normal growth temperatures.

We would like to comment on the correction of Eq. (6) if the solid solution is not ideal. In that case, different arrangements of the atoms would have slightly different energies. Since the number of different arrangements of atoms (configurations) is very large, we may assume that it has a Gaussian energy distribution, with average μ and standard deviation σ, which depend on the composition. Now, it is rather straightforward to use this Gaussian distribution to obtain both μ and S as functions of temperature:

$$\mu(T) = \mu(T = \infty) - \frac{\sigma^2}{kT} , \tag{8}$$

and

$$S(T) = S_{\text{ideal}} - \frac{1}{2} k \left(\frac{\sigma}{kT}\right)^2 , \tag{9}$$

where S_{ideal} is given by Eq. (6). It should be noted here that the expressions (8) and (9) should be viewed as asymptotic expansions, correct only in the limit of high temperature. Expressions such as Eqs. (8) and (9), as well as higher order terms, were given by Hildebrand and Scott.[7] It should be noted that σ vanishes at the endpoints of the composition range ($x = 0$ or $x = 1$) and attains a maximum in between. At this maximum $\partial^2(\sigma^2)/\partial x^2 < 0$. Therefore, the correction to the free energy of mixing due to finite temperatures in Eqs. (8) and (9) has a positive curvature, thus enhancing mixing

TABLE I. Elastic constants times the volume of a formula unit for various III–V semiconductors (in units of eV). $C_{(100)}$ and $C_{(111)}$ were defined in Eq. (2). From this table it seems that a value of 100 eV has the right order of magnitude for the III–V semiconductors.

Material	$C_{(100)}$	$C_{(111)}$
GaP	74.9	103.7
InP	59.9	94.4
GaAs	69.6	97.6
InAs	53.2	83.5
AlSb	60.6	87.0
GaSb	62.0	86.5
InSb	53.7	82.5

rather than separation. The magnitude of these correction terms is usually small.[7]

The enthalpy of mixing term is the one that poses the main difficulty. It has to have a magnitude of more than a few tens of meV to dominate in temperatures of a typical crystal growth. The enthalpy of mixing in most ternary (pseudobinary) III–V alloys is usually approximated[8] by regular solution theory:

$$\Delta H^m = \alpha x(1-x), \tag{10}$$

where α is an interaction parameter. Experimental estimates of α in Eq. (10) for several III–V ternary systems are given by Panish and Ilegems.[8] Various phenomenological models, using several unknown parameters, were used to obtain these values. The uncertainty in the accuracy of these parameters, therefore, is still unknown. Stringfellow[9] has observed a scaling of α in Eq. (10) like the square of the mismatch in most III–V alloys. Martins and Zunger[10] showed that such a scaling is expected on theoretical grounds from the strain component of ΔH^m. They have further showed that the chemical effects, due to charge transfer between bonds, do not scale with Δa^2, but for random alloys this contribution is small.

We shall now discuss the contribution of the elastic strain in the film. The excess energy due to elastic strain in the film, induced by the substrate, is given by Eq. (3). To calculate this term, we have to know the elastic constants of the alloy for the whole composition range. Such a complete set of data has not been measured for any of the III–V ternary systems. We can, however, estimate the magnitude of this term.

We assume that the second derivative of $\frac{1}{2}C(x)x^2$ with respect to x is of the same order of magnitude as $C(x)$. This assumption is equivalent to assuming that there are no "spikes" in $C(x)$. To estimate this value, we present in Table I the relevant elastic constants, $C_{(100)}$ and $C_{(111)}$ for several binary III–V semiconductors. These elastic constants were calculated [using Eq. (2)] and later multiplied by the volume of a formula unit ($a^3/4$) to obtain the value of the elastic constants per formula unit. From Table I, it follows that $C(x)\cdot a^3/4$ is on the order of 100 eV per formula unit. Multiplying this value by the square of the strain, we obtain that the elastic strain contribution to the free energy is on the order of 0.1 meV per formula unit when the mismatch is 0.1%, 10 meV per formula unit when it is 1%, and up to 1 eV when the mismatch is 10%.

Only when the mismatch between the film and the substrate is on the order of several percent, the strain term is appreciable (on the order of 10–100 meV). It may still be smaller than the entropy-of-mixing term, but when the entropy-of-mixing term is nearly balanced by the enthalpy of mixing, the strain can make the difference.

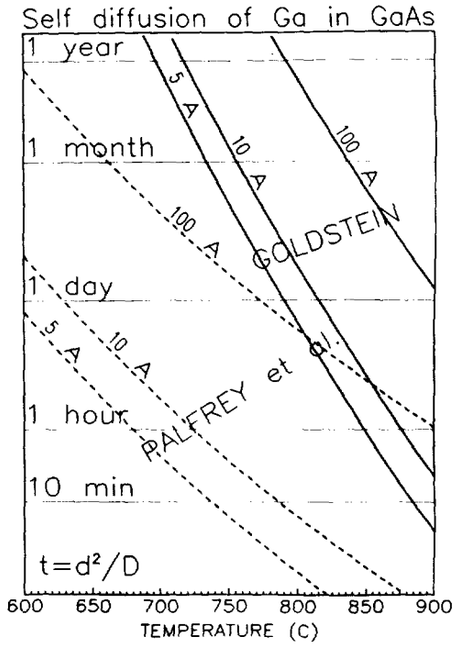

FIG. 1. Characteristic self-diffusion times of Ga in GaAs according to the experimental data of Goldstein (Ref. 13, solid lines) and Palfrey *et al.* (Ref. 14, dashed lines). The time required to diffuse over characteristic distances of 5, 10, and 100 Å is shown vs temperature.

For a precise calculation, one has to know both the elastic constants of the film material as a function of composition and the thermodynamical data. At present, the elastic constants of the alloys have not been measured, and there is a lot of uncertainty about the thermodynamical functions of these alloys (see our discussion of $Al_xGa_{1-x}As$, which is one of the best characterized alloys, in the following section). We, therefore, cannot hope at this moment to make any definite statements, only to point at some alloy systems that could prove to be interesting.

We are interested in systems that have a large mismatch (1%–10%), and a large, positive enthalpy of mixing. Among the ternary III–V systems, these two properties are correlated[9] since the chemical contribution to the enthalpy of mixing is usually small for random alloys.[11] The four ternary III–V systems that include InSb are of particular interest, since they all satisfy the large mismatch condition. In addition, In(As, Sb) is a candidate for strained layer superlattices with small band gaps that may be used as IR materials.[12]

IV. $Al_xGa_{1-x}As$ on GaAs

In this section we estimate the relevant parameters for the $Al_xGa_{1-x}As$ on GaAs interface. Since the experimental data is incomplete, we have to estimate several parameters based on theoretical considerations.

A. Kinetics

Knowing the kinetics of the system could help clarifying

whether the clustering in $Al_xGa_{1-x}As$ is stable or metastable. Unfortunately, only partial self-diffusion data are available for the $Al_xGa_{1-x}As$ system, and they are mainly high temperature data. In Fig. 1, we show characteristic times for self diffusion of Ga in GaAs vs temperature. There are two sets of curves in Fig. 1, corresponding to diffusion data of Goldstein[13] and of Palfrey *et al.*[14] In each set there are three curves, corresponding to diffusion over characteristic distances of 5, 10, and 100 Å. The relation between diffusion distance (d) and diffusion time (t) was calculated according to

$$t = d^2/D, \tag{11}$$

where the diffusion coefficient D is given by

$$D = D_0 \exp\left[\frac{-Q}{kT}\right], \quad \begin{array}{ll} D_0 = 1\times10^7\ \mathrm{cm^2\,s^{-1}}, & Q = 5.6\ \mathrm{eV}, \text{ (Goldstein[13])} \\ D_0 = 3.9\times10^{-5}\ \mathrm{cm^2\,s^{-1}}, & Q = 2.6\ \mathrm{eV}, \text{ (Palfrey } et\ al.\text{[14])}. \end{array} \tag{12}$$

(The discrepancy between the two sets of data was attributed by Palfrey *et al.* to the difference in As overpressure during growth.) One can easily see in Fig. 1, that nonequilibrium features as narrow as 5 Å would require about a day of anneal at 800 C to dissipate, if we take Goldstein's data as representing the actual diffusion rates. This would imply that the features as large as those observed by Petroff *et al.*[3] do not have enough time to equilibrate. On the other hand, if Palfrey's data represent the actual diffusion rates, then at 800 C it will take only few minutes to establish quasiequilibrium on a 5 Å scale and several hours to establish quasiequilibrium on a 100 Å scale. In that case the features observed by Petroff *et al.* could be formed spontaneously from a uniform alloy if they are more stable.

The large discrepancy between the two sets of self-diffusion data, as well as lack of self-diffusion data of $Al_xGa_{1-x}As$, does not enable us to determine whether thermal equilibrium was established based on annealing time. We, therefore, have to determine if the clustered alloy is more stable than the uniform alloy, based on energy considerations.

B. Thermodynamics

In our treatment we would like to use the ideal-solution expression for the entropy of mixing. Recent experimental[15] and theoretical[11] papers have questioned the ideality of $Al_xGa_{1-x}As$ grown at the 600–800 °C range. We may have to correct the entropy of mixing to account for nonideality, but it was shown in the previous section that such a correction, at least to first order in $1/T$, would enhance mixing rather than separation. Assuming that the $Al_xGa_{1-x}As$ solid is an ideal solution,[16] the entropy of mixing was given in Eq. (6). The entropy contribution to the second derivative of the free energy is at least $4NkT$, which is 300 meV per formula unit at 600 °C. We will show that it is almost an order of magnitude larger (in absolute value) than the contributions of the enthalpy of mixing, hence, dominating the mixing properties of $Al_xGa_{1-x}As$ above 600 °C.

The enthalpy of mixing of random $Al_xGa_{1-x}As$ has been estimated to be zero, or very close to zero. These estimates were, however, based on high-temperature measurements. Foster *et al.*[16] have investigated the solidus line of the $Al_xGa_{1-x}As$ system and concluded that this system is ideal [i.e., $\alpha = 0$ in Eq. (10)]. Stringfellow[9] also concluded that $\alpha = 0$ in the $Al_xGa_{1-x}As$ system. Other figures quoted in the literature are $\alpha = -500$ cal/mol[8] at 1000 °C, $\alpha = +400$ cal/mol[1] at 700 °C, and $\alpha = -3892 + 4T$ cal/mol[1] for 1073 K $< T <$ 1273 K. (1 kcal/mol = 43.3 meV/formula unit). The experimental figures, therefore, are somewhere in the range

$$|\alpha| = < 25\ \text{meV/formula unit}, \tag{13}$$

and were obtained by fitting the phase diagram of $Al_xGa_{1-x}As$. To obtain yet another estimate of α, we have performed *ab initio* self-consistent calculations on As-(Ga, Al)$_4H_{12}^{3-}$ clusters. Our calculations (to be described below) give an estimate of α which is included in the experimental range given in Eq. (13) in the separating region ($\alpha > 0$), but extends beyond the experimental range in the mixing region ($\alpha < 0$).

Our calculations were performed as follows. Self-consistent generalized-valence-bond[17] formalism was used to calculate the total energy of $AsGa_4H_{12}^{3-}$, $AsGa_2Al_2H_{12}^{3-}$, and $AsAl_4H_{12}^{3-}$ clusters. The quasichemical interaction was calculated according to

$$\Omega = E_{AsGa_2Al_2} - \frac{E_{AsGa_4} + E_{AsAl_4}}{2}. \tag{14}$$

In Eq. (14), $E_{AsGa_2Al_2}$ is the total energy of the $AsGa_2Al_2H_{12}^{3-}$ cluster, etc.

All the clusters in our calculations consisted of a central arsenic atom surrounded by a shell of four cations (either gallium or aluminium atoms), which was in turn surrounded by a shell of 12 hydrogen atoms. The hydrogen atoms were used to terminate the dangling bonds of the cations. The angles between the bonds formed by each atom and its nearest neighbors were kept tetrahedral (109.47°) throughout the calculation. The clusters had a net charge of 3- to ensure covalent bonding similar to that in the crystal. The aluminum, gallium, and arsenic atoms were represented by a double-ζ basis set, containing s- and p-like wave functions. The hydrogen atoms were represented by a single, s-like wave function (a minimal basis set). The distances between the hydrogen atoms and their neighbor cation atoms were kept at a prescribed value of $d_m = 2.35$ Å, rather than at the optimal distance, and the hydrogenic wave functions were inflated by a factor of $r_H = 2.5$. These two parameters, r_H and d_m, were used to control the electronegativity of the hydrogenic shell[18] (that was used to mimic the bulk $Al_xGa_{1-x}As$).

The value of Ω in Eq. (14) depends on the individual Ga–As and Al–As bond lengths. In Fig. 2 we show the total energy of the $AsGa_2Al_2H_{12}$ cluster (dashed curves) and Ω of Eq. (14) (continuous curves) as contour maps in the plane of Ga–As vs Al–As bond lengths. One can observe in Fig. 2 that a value of

$$-0.020 < \Omega < +0.004\ \text{eV} \tag{15}$$

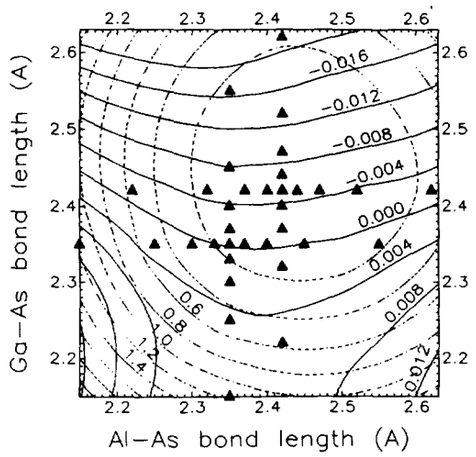

FIG. 2. Total energy of the $AsAl_2Ga_2H_{12}^{3-}$ cluster (dashed lines), and the quasichemical interactions, (Ω) (solid lines) as a function of the Ga–As and Al–As bond lengths. The interaction parameter Ω was calculated using Eq. (14). It is acting toward phase separation when positive and toward phase mixing or compound formation when negative. Its value is rather small for all reasonable values of the bond lengths, in good agreement with Eq. (13). Solid triangles represent the values that were actually calculated (using generalized valence bond method). The values between the triangles were interpolated.

is obtained for all reasonable values of the Ga–As and Al–As distance. The Ω calculated in Eq. (14) include all the bonds between one anion and its neighboring cations. The relation between Ω in Eq. (14) and α in Eq. (10), was calculated using the quasichemical model.[7] We assume that the contribution to the excess enthalpy of mixing is given by Ω from each arsenic atom that is bonded to two gallium and two aluminum atoms; $\Omega/2$ from each arsenic atom that is bonded to one cation of one kind, and three of the other kind, and 0 from each arsenic atom that is bonded to four cations of the same kind. If we further assume that all the configurations of cations are equally probable [$T=\infty$ in Eq. (8)], then the enthalpy of mixing per formula unit for the random alloy is given by

$$\Delta H^m = \binom{4}{0}x^4\cdot 0 + \binom{4}{1}x^3(1-x)\frac{\Omega}{2} + \binom{4}{2}x^2(1-x)^2\cdot\Omega + \binom{4}{3}x(1-x)^3\frac{\Omega}{2} + \binom{4}{4}(1-x)x^4\cdot 0 = 2\Omega\cdot x(1-x)(1+x-x^2). \quad (16)$$

The polynomial $(1+x-x^2)$ varies between 1 and 1.25 in the range $0<x<1$. Therefore, by comparing Eqs. (16) to (10), it follows that α ranges between 2 and 2.5 Ω, using this model. Therefore, our calculations yield a value of α in the range $-50<\alpha<+10$ meV per formula unit. This estimate is included in the experimental estimate given in Eq. (13) in the separating ($\alpha>0$) range, but extends it somewhat in the mixing ($\alpha<0$) range.

We now take the second derivative of the enthalpy of mixing in Eq. (10) with respect to the concentration x to obtain a value of -2α per formula unit, which is more than -50 meV per formula unit, using both our calculations and the experimental data. This is almost an order of magnitude smaller than the 300 meV contributed by the entropy of mixing. Our calculations, therefore, suggest that there is no miscibility gap in the $Al_xGa_{1-x}As$.

We would also like to comment here about the formation of an ordered compound ($Al_{0.5}Ga_{0.5}As$) as was reported recently by Kuan *et al.*[15] Such a compound will be thermodynamically stable if the gain in enthalpy of mixing more than offsets the loss in entropy of mixing. According to the quasichemical model described above, the enthalpy of mixing of such an ordered compound is Ω per formula unit, compared to $\frac{5}{8}\Omega$ of the random alloy of the same composition. [$\frac{5}{8}\Omega$ is the value of Eq. (16) at $x=\frac{1}{2}$]. The gain in enthalpy of mixing is, therefore, $\frac{5}{8}\Omega$ per formula unit, according to this model. The entropy of mixing of the compound vanishes due to the ordering, while the entropy of mixing of the alloy equals $-k\log\frac{1}{2}$, representing a free energy loss of about $0.7kT$, which is approximately 50 meV per formula unit at 600 °C, compared to enthalpy gain of $\frac{5}{8}\Omega$ which is at most 7.5 meV according to our calculations. Srivastva *et al.*[11] have suggested that charge transfer from the weaker Ga–As bonds to the stronger Al–As bonds may result in a negative enthalpy of mixing, which in turn results in compound formation at low temperatures. Our calculation of Ω described above agree with the sign of the enthalpy suggested by Srivastva *et al.*, but the critical temperature required for such compound formation is, according to our calculations, much lower than 600 °C. Our calculations, therefore, suggest that the ordered structure observed by Kuan *et al.*[15] may not be the equilibrium state of $Al_xGa_{1-x}As$.

Finally, the elastic constants of $Al_xGa_{1-x}As$ as a function of x have not been measured experimentally. Fortunately, the strain in an $Al_xGa_{1-x}As$ film grown on GaAs is so small that we can easily establish the fact that the strain contributes less than 1 meV/formula unit to the total free energy. The difference in lattice parameters between GaAs and AlAs is extensively documented in the literature. Ettenberg and Paff[19] showed that the mismatch varies between 0.14% at room temperature, to 0.0% at approximately 950 °C. We can, therefore, assume that above 600 °C,

$$\left(\frac{\Delta a}{a}\right)^2 < 10^{-6}. \quad (17)$$

The contribution of the strain for such a small mismatch was estimated in the previous section to be on the order of 0.1 meV per formula unit. Even if we allow an order of magnitude error in the estimate of the second derivative of $C(x)\cdot x^2$, the contribution of the strain is still at most 1 meV. Such a small contribution cannot affect the miscibility properties, unless the enthalpy of mixing and the entropy-of-mixing terms exactly cancel. This was shown not to be the case.

V. SUMMARY AND CONCLUSIONS

In this paper we have investigated the effect of substrate-induced strain on the miscibility properties of an epitaxial film consisting of an alloy. This investigation was motivated by the observed alloy clustering in $Al_xGa_{1-x}As$ grown epitaxially on GaAs. We have shown that in some cases the miscibility properties of the film can be reversed by the strain induced by the substrate. A miscibility gap could be opened

in the film even if no such gap exists in the bulk alloy, and conversely, a miscibility gap in the bulk alloy could be closed by the strain.

The substrate-induced strain in the film is small for alloys that are closely matched to the substrate. For a mismatch of 0.1%, for example, we have estimated the strain effect to be only a fraction of a meV per atom (in the case of III–V ternary alloys). For a larger mismatch, say 1%, the contribution to the free energy is on the order of 10 meV/molecule. This contribution is still too small to offset the entropy of mixing at typical epitaxial growth temperatures. In cases in which the entropy of mixing is nearly balanced by the enthalpy of mixing, however, the strain term could tip the balance. We have suggested that this effect may be important in strained layer superlattices based on In(As, Sb). Since strained-layer superlattices are grown at relatively low temperatures, miscibility gaps may be present in In(As, Sb) alloys. It would be of great technological interest to find whether the strain can lower the critical temperature of the miscibility gap, or alternatively, enhance directional phase separation. Currently, lack of elastic data regarding these alloys as well as uncertainty about the thermodynamical data prohibit any serious attempt to calculate these effects.

We have also investigated the $Al_x Ga_{1-x} As$ on GaAs system. In that case we have concluded that the strain is too small to affect the miscibility. Since clustering was observed in this system, and we concluded that strain effects could not have caused it, we have examined the thermodynamical data in more detail. We have performed *ab initio* calculations of the enthalpy of mixing $Al_x Ga_{1-x} As$ and concluded that $\partial^2 H_m/\partial x^2$ is about an order of magnitude smaller than $\partial^2 TS_m/\partial x^2$ at the normal growth temperature ($T > 600$ °C). Our calculations are supported by the experimental data of Foster *et al.*[16] which indicate that the $Al_x Ga_{1-x} As$ system behaves as a nearly ideal solution. In light of this big difference between the contributions of the enthalpy and entropy of mixing, the very small additional term due to strain cannot open a miscibility gap. It seems likely, therefore, that the uniform random alloy is the most stable state of the $Al_x Ga_{1-x} As$ system at temperatures above 600 °C. We attribute the fact that clustering was observed in that system to the slow kinetics at 600–800 °C.

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[1] H. C. Casey, Jr. and M. B. Panish, *Heterostructure Lasers* (Academic, New York, 1978).
[2] N. Holonyak, Jr., W. D. Laidig, B. A. Vojak, K. Hess, J. J. Coleman, P. D. Dapkus, and J. Bardeen, Phys. Rev. Lett. **45**, 1703 (1980).
[3] P. M. Petroff, A. Y. Cho, F. K. Reinhart, A. C. Gossard, and W. Wiegmann, Phys. Rev. Lett. **48**, 170 (1982).
[4] N. A. Goryunova, F. P. Kesamanly, and D. N. Nasledov, in *Semiconductors and Semimetals, Vol. 4*, Physics of III–V Compounds, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1968), p. 416.
[5] S. K. Maximov, Phys. Status Solidi A **83**, 685 (1984).
[6] J. H. van der Merwe and C. A. B. Ball, in *Epitaxial Growth, Part B*, edited by J. W. Matthews (Academic, New York, 1975), Chap. 6.
[7] J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes* (Reinhold, New York, 1950), p. 146.
[8] M. B. Panish and M. Ilegems, *Progress in Solid State Chemistry*, edited by H. Reiss and J. O. McCaldin (Pergamon, New York, 1972), Vol. 7.
[9] G. B. Strinfellow, J. Phys. Chem. Solids **34**, 1749 (1973).
[10] J. L. Martins and A. Zunger, Phys. Rev. B **30**, 6217 (1984).
[11] G. P. Srivastava, J. L. Martins, and A. Zunger, Phys. Rev. B **31**, 2561 (1985).
[12] G. C. Osbourn, J. Vac. Sci. Technol. B **2**, 176 (1984).
[13] B. Goldstein, Phys. Rev. **121**, 1305 (1961).
[14] H. D. Palfrey, M. Brown, and A. F. W. Willoughby, J. Electrochem. Soc. **128**, 2224 (1981).
[15] T. S. Kuan, T. F. Keuch, W. I. Wang, and E. L. Wilkie, Phys. Rev. Lett. **54**, 201 (1985).
[16] L. M. Foster, J. E. Scardefield, and J. F. Woods, J. Electrochem. Soc. **119**, 765 (1972).
[17] F. W. Bobrowicz and W. A. Goddard, III, in *Modern Theoretical Chemistry: Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. III, p. 79.
[18] A. Redondo, W. A. Goddard, III, C. A. Swarts, and T. C. McGill, J. Vac. Sci. Technol. **19**, 498 (1981).
[19] M. Ettenberg and R. J. Paff, J. Appl. Phys. **41**, 3926 (1970).